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INVESTIGATION OF METHODS TO IMPROVE THE LOW TEMPERATURE CHARGE ACCEPTANCE OF LEAD-ACID BATTERIES

by
E.M.L. Valeriote



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INVESTIGATION OF METHODS TO IMPROVE THE LOW TEMPERATURE
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Eugene M.L. Valeriote

Energy Conversion Division

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OCTOBER 1979
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*Presently employed at Cominco Ltd., Sheridan Park, Ontario.

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ABSTRACT

Investigation of the causes of poor low temperature charge acceptance of the lead acid battery at DREO has been primarily directed towards understanding and improving positive electrode characteristics. However, studies of the negative electrode, of electrolyte and electrode additives, of electrolyte composition, and of charging and heating methods for improving charge acceptance are also discussed.

Previous research and recent advances are reviewed. Possible improvements are suggested. Recommendations for further research and development are made, based on the encouraging results of the current work and on the accumulated knowledge represented by the work reviewed.

RÉSUMÉ

On examine les causes du faible pouvoir de charge des accumulateurs au plomb à basse température en essayant particulièrement de comprendre et d'améliorer les caractéristiques de la plaque positive. On analyse l'étude du CRDO, subventionnée par la MDN, et d'autres études portant sur l'électrode négative, l'électrolyte, les produits chimiques des plaques, la composition de l'électrolyte et les méthodes de charge et de chauffage. On passe en revue les recherches antérieures et les innovations récentes. En s'appuyant sur des résultats prometteurs et sur les nouvelles connaissances acquises jusqu'à présent, on propose des perfectionnements éventuels et on oriente les recherches et les développements à venir.

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INTRODUCTION

For reasons that are perhaps only beginning to be understood, the lead acid battery, at very low temperatures ($< -20^{\circ}\text{C}$), is incapable of accepting recharge at operationally acceptable rates. When a 6 cell (12V) battery at -40°C is charged at a constant voltage in the range of 14V to 16V (2.33 to 2.6V/cell), the charging current falls to less than the C/100 rate within a few minutes. Even low-rate charging (C/20) at constant current causes a rapid increase of voltage to above 15V without restoration of all the previous discharge and further charging becomes very inefficient. Only part of the total current at high voltages results in the storage of recoverable energy, the remainder being consumed in gas evolution or other parasitic side reactions. As a consequence, expensive methods of heating batteries are required for very cold weather operation or (as happens in many cases) vehicles are left running overnight out of fear of not being able to restart them in the morning.

HISTORICAL PERSPECTIVE

The earliest substantial research directed towards determining the cause of the poor charge acceptance of the lead acid battery at -40°C , appears to have been carried out at Gould-National under contract to the U.S. Army Signal Corps Engineering Laboratories (1). This work was recently re-interpreted and reported by Willihnganz (2). He found that the negative plate charge acceptance rate at -40° was sensitive to blockage by components of the organic expander and that at the start of charge, following a shallow (4%) discharge, the negative plate was limiting charge acceptance. However, very soon thereafter the positive plate (which was less well understood) became limiting and was therefore most in need of investigation and improvement.

There was some evaluation work, some studies of negative plate organic expanders (3) and of the temperature dependence of lead passivation (4) done at DREO (then DRCL) prior to 1960 (5), but research directed towards the low temperature charging problem (6) was concerned mainly with determinations of lead sulphate conductivity, which, it was concluded, were not related to the temperature dependencies observed. A limited amount of coulometric work indicated the possibility of the storage of energy at low temperatures which was only recoverable when the cell was warmed. The phenomenon was tentatively ascribed to formation of peroxides which accumulated in the electrolyte at low temperatures and was available for subsequent discharge (6). Later

investigations, both at DREO (7) and elsewhere (8,9,10), demonstrated that persulphate formation occurred in sulphuric acid solutions both on Pb anodes (7-9) and on Pt (10), the yield depending on temperature, current density and acid concentration (7). A very limited amount of work, specifically directed toward studying very low temperature ($<-20^{\circ}\text{C}$) performance, was done between 1960 and 1970 (11-15). While a few workers attempted to determine the affect of temperature on charge acceptance (11b,12) as Willihnganz had done earlier (2), the more usual concern was with the temperature dependence of discharge performance (13,15) of batteries which had previously been charged at room temperature.

ORIGINS OF CURRENT WORK

During a seminar on lead acid batteries held at DREO in 1967 (11), Luciani recommended that future DND emphasis should be on improvement of low temperature charge acceptance of lead acid batteries (11b). This was followed eventually by a recommendation to DRB "that the EPS Division study ways and means of alleviating the problem of low temperature charge acceptance and.... recommend an appropriate research program to achieve this objective" (16). Following a literature search, technical and consultative sessions at DREO (August and 7 December, 1972) and a statement of the military requirements (17), a text in support of research for improved low temperature performance of lead acid batteries or for a suitable replacement was forwarded to Chairman/DRB from Chairman/AC(EPS) (18).

Preliminary research began at DREO as an extension of a study of lead reactions in chloride media, related to seawater batteries. Formal tasks 27140 and 27141 were instituted specifically for low temperature lead acid research in the last quarter of 1973 (19). The in-house work (Current Task Numbers 25A21, 25A28, 25A70 and 25A71; the first two are sponsored tasks DLMSEM 10 and DLMSEM 17 respectively) was complemented by contracted research at Gould Manufacturing, Fort Erie, Ontario (20) and at Cominco Product Research Centre, Mississauga, Ontario (21,22) and in various university laboratories with the aid of DRB Research Grants (23). Some of the early work has already been reviewed (24).

What has been learned, and what progress has been made during these three and one-half years, since DREO undertook to "improve the low temperature charge acceptance capability of the lead acid battery" (19)?

REVIEW OF PROGRESS (TO MAY 1977)

STATEMENT OF THE PROBLEM

Luciani (11b) stated that the poor performance resulting from deterioration of the discharge performance of lead acid batteries at low temperatures could be circumvented by specifying adequate capacity to supply high cranking currents, and possibly by some form of battery heating if still further improvements were necessary. He further concluded that one of the factors contributing to the poor low temperature lead acid performance was its inability to accept a charge.

Similar conclusions were reached by VARTA Batteries AG (25). They showed that a 100 Ah battery (NATO Battery 6N11 - equivalent to BB248U), which had been fully charged at room temperature, yielded about 11 Ah at the 3C rate (2.25 minutes cranking) at -40°C ; that the same battery yielded 6 Ah (1.2 minutes) if it was only 90% charged; and 3.5 Ah (0.7 minutes) if 75% charged. Thus it is important to assure that a vehicle battery remains fully charged to assure cold weather starting. One reason for this is resistance increases more quickly with decrease in temperature for a partially charged battery than for a fully charged one (25).

In the work of the U.S. Army Signal Corps (1), it was pointed out that even disconnecting the voltage regulator of the vehicle, so that the applied battery voltage rose to 2.9V/cell or higher and the battery gassed freely, did not result in an immediately effective rate of recharge although eventually sufficient heat was produced to increase the internal temperature and thus facilitate recharge.

It is important to note that work at DREO (26) and elsewhere (1,12) shows that complete recharge of a battery at -40°C is possible at very low rates ($<0/100$). It is therefore the rate of charge acceptance and not charge acceptance per se which requires improvement. Ideally it should be possible to completely recharge the battery at a specified low temperature (say -40°C) within the period of time (say 1 hour) that the vehicle (and therefore its charging system) would be expected to be operating, following battery discharge.

Thus it appears that, although improvement of the low temperature discharge characteristics of the lead acid battery would be desirable, a more important problem is improvement of its rate of charge acceptance.

POTENTIAL SOLUTIONS

When the task was begun, the fundamental cause of the problem was not known, although obviously the essential factor, without which no problem would exist, is a cold internal battery temperature. Thus there appeared to be only one solution known to be effective with any certainty viz. - the application of heat. This approach had been tried but without very satisfactory results due to associated problems, although one such method now seems very promising as discussed below. This and other potential approaches can be categorized as falling into one of two groups: one which treats the battery as a "black box" and acts on the system as a whole and one which treats one or more individual components of the system and tries to identify and correct the "bottle necks" to low temperature performance.

For either of these approaches to be effective however, some understanding of the processes involved in the charge and discharge reactions is necessary and this understanding is very limited. The following factors, and assessments of their importance, therefore entered into the planning of the research program.

BLACK BOX TREATMENT

Internal heating of the battery is the most obvious and definite solution. The difficulty is in introducing the heat quickly. This constraint eliminates methods which rely on heat transfer through the case of a cold-soaked battery, because of its low thermal conductivity and the high heat capacity of both case and electrolyte. Various methods of introducing heat have been proposed or tried. For example, heat can be introduced by means of tubes built into the battery case, into which removable heaters could be placed (27), or built-in cell heaters (28) would involve specially designed and constructed batteries and would be expensive.

Methods of introducing heat without modifications to the battery itself have also been developed:

A system of ac heating was developed by Lucas (Batteries) and Retox Ltd. for the U.K. Chiefton Tank (29). Approximately 400 watts/battery were required to heat the four 6TN (BB248U) batteries at the rate of 1°C/rpm on the vehicle auxiliary DC generator. The system was only applicable to multiple battery units since its principle of operation relied on a battery thermal analogue, which was sandwiched between two batteries. The 1975 production cost of equipment for heating four 6TN batteries was approximately 1500 pounds Stirling (30).

Another method was developed by VARTA AG (25), also for four 6TN batteries, which could also be applied to single batteries. This system has been specified for the German Leopard II Battle Tank (31). The principle of operation is induction of eddy currents in the grids of normal batteries by an alternating current applied to primary windings, in the walls of an insulated box built to accommodate the battery. The heat (200-300 watts/battery) is thus applied directly to the interior of the plates, where it is most effective because it causes a rapid temperature increase of the active material due to the low heat capacity of the plates. Work at DREO, to be discussed below, indicated that the barrier to charge acceptance is probably a limitation within the pores of the plates, which would be among the first components of the battery to feel the effects of the inductive heating. The effect of the inductive heating, which can be applied before or during charging, is immediate and dramatic in increasing the charge current at very low temperatures (25). The price quoted (August 1975) for one unit for controlled heating of 4 batteries was 7350 DM, half of which was for the 900 W (4 battery) d.c. to a.c. inverter. This equipment appeared to be the simplest and most effective and required the least energy of those assessed. An insulated wound battery box (Temperierkästen) was received in late April 1977, for evaluation at DREO.

Another method proposed to improve low temperature charge acceptance (11b) was a pulse charging technique. This was examined under contract (20-22) and will be discussed later.

IDENTIFICATION OF LIMITING COMPONENT(S)

The lead acid battery is not really just a black box but an extremely complex system of components. Success in improving performance via the black box approach, depends on finding a solution which improves the limiting component(s) without causing an unacceptable deterioration in performance of other components. Thus magnetic induction heating must be regulated, lest it cause undue grid corrosion or loss of electrolyte through overheating. The components of the battery are the case, metallic conductors, electrolyte, separators and the conductive supporting grids and active materials which make up the positive and negative plates. The positive plate itself is porous and unusually complex, consisting of at least 10 compounds or alloys of Pb in the solid phases: the Pb alloy of the grid, two crystalline modifications of both PbO and PbO_2 , $PbSO_4$ and the basic sulphates $nPbO \cdot PbSO_4$ for which $n = 0, 1, 2, 3$ and 4 ; as well as the electrolyte constituents in the pores. Where in such a complicated system is the limit to low temperature charge acceptance likely to be?

It is unlikely to be related to the case; the effects of cell geometry or interactions of components required a better basic understanding of the mechanisms of reaction and of the role of individual components; separators were a possibility, but the effects of separators could be determined by later comparison of half cell and full cell characteristics. This left the electrolyte and the positive and negative plates for consideration in depth.

THE ELECTROLYTE

Between room temperature and -40°C , the resistance of 35% sulphuric acid increases by a factor of about 7 (32) but the resistance of a fully charged battery increases by a factor of only about 2.3 (25). Viscosity of the acid increases by a factor of about 15 (32). The electrolyte resistivity and viscosity variations with temperature have been plotted in Figure 1 in such a way as to obtain values of activation energies for the associated transport processes. At temperatures above 0°C , energies of activation of 2.9 and $4.1 \text{ kcal mol}^{-1}$ are obtained from the resistivity and viscosity data respectively. Both these values are of the expected order of magnitude for diffusion in solution. The higher average values, of 4.5 and $6.9 \text{ kcal mol}^{-1}$ respectively, for these parameters (and the increasing non-linearity of the plot) at lower temperatures, suggest that some change of transport mechanism occurs below 0°C . The activation energies are still in the range possible for diffusion in solution but probably involve different diffusing species.

If changes of electrolyte resistance were the only cause of poorer low temperature charge acceptance, one might expect that it could be remedied by simply charging at higher voltages. This approach had already been found ineffective (1) but is being re-examined in the current work (26). Resistance effects, other than that due to electrolyte resistance, must also be important, in view of the smaller rate of increase of total cell resistance in comparison to electrolyte resistance. The temperature dependence of electrolyte diffusion properties was studied at DREO, as part of the electrode study, by using rotating disc electrodes to determine the relative importance of diffusion effects during recharge, and will be discussed further below. The effect of a number of electrolyte additives, on low temperature charge acceptance of positive electrodes (21,22,23) and of batteries (20) was examined, although previous efforts to find a beneficial additive (1,2) had been unsuccessful. These studies were not aimed at electrolyte modification; relatively small quantities of additives were usually involved. They were part of an effort to find methods of introducing agents which might favourably modify the electrochemical characteristics of the electrode.

Persulphate formation at Pb electrodes during anodization at low temperatures was also investigated (7). Faradaic efficiencies for persulphate formation were found to increase with acid concentration and with decreasing temperatures.

Finally, the solubility of lead sulphate in sulphuric acid was determined as a function of temperature from $+25^{\circ}\text{C}$ to -50°C since it had been suggested (2,13,42) that both electrode reactions were related to the solution rate of lead sulphate and that the precipitation or dissolution of PbSO_4 was controlled by its solubility (2).

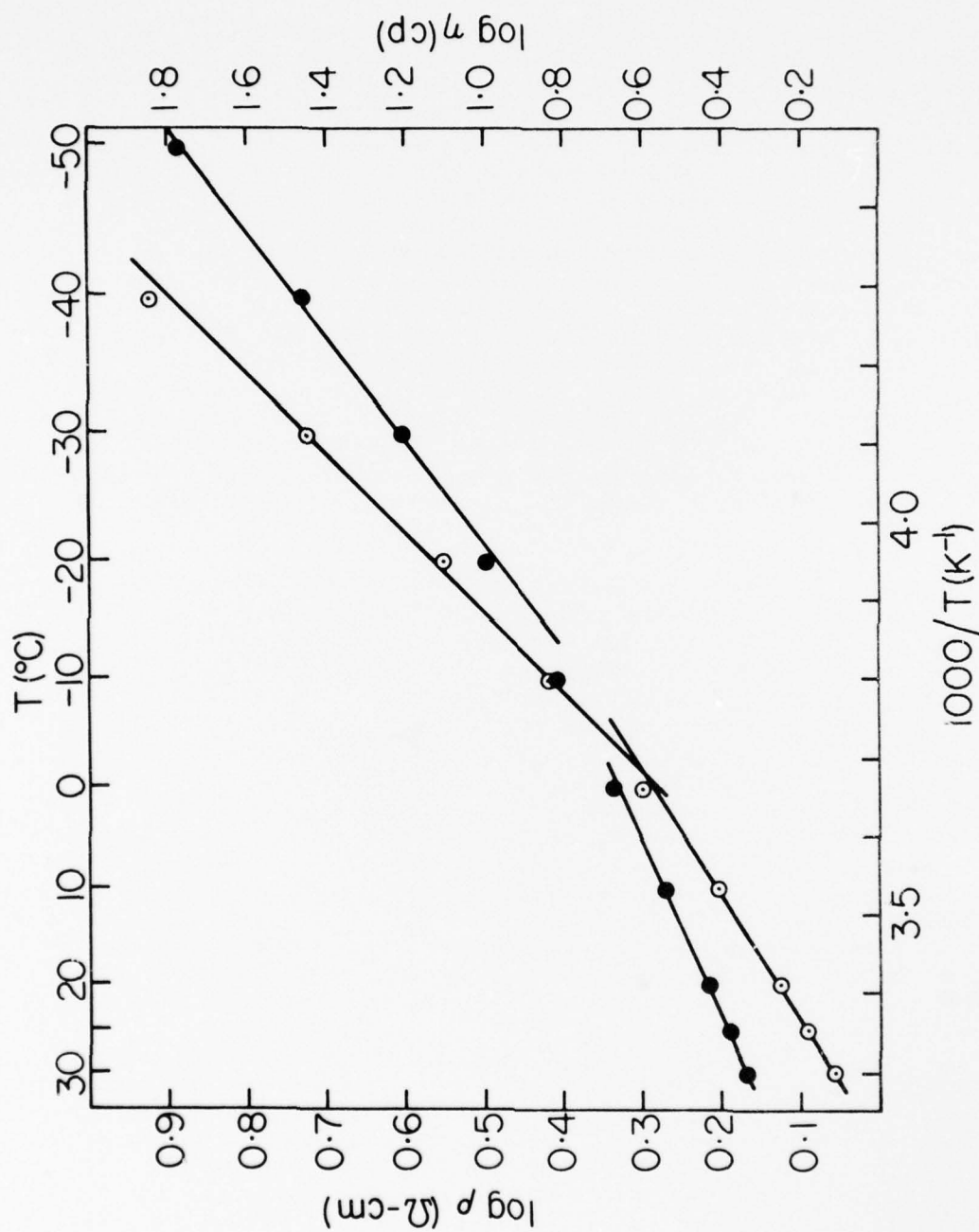


Fig. 1: Arrhenius plots of sulphuric acid electrolyte resistivity, \bullet , for 35% acid and of viscosity, \circ , for 40% acid as a function of reciprocal temperature (32).

NEGATIVE AND POSITIVE PLATES

Based on the earlier work (1), Willihnganz concluded (2) that at the beginning of recharge at low temperatures, charge acceptance was limited by the negative plate. He attributed the poor rate of charge acceptance of negative plates to an adsorbed barrier layer, probably a hemicellulose. This may have been present as an impurity in crude lignin sulphonic acid, an organic expander, which was originally added to the negative plates to increase low temperature capacity. Extraction of the impurities with sulphuric acid left a purified lignin sulphonic acid which remained beneficial to low temperature capacity but interfered with charge acceptance much less than the impure expander.

Although the negative plate was found to be limiting at the start of recharge, Willihnganz also found (2) that the positive plate became limiting very soon after for a battery discharged by only a few percent of its room temperature capacity. The reasons for the poor positive plate charge acceptance were not clear and he concluded that, since the work seemed to indicate a method for solving the negative plate problem, further work should be devoted to understanding the reasons for poor positive plate charge acceptance.

Later work by Berndt (13) showed that the charging efficiency of the negative plate depended more strongly on charging current density and on temperature (at low temperatures) than did that of the positive plate. However, Berndt's plates were only recharged to a 50% state of charge, following a deep discharge, to avoid the complications of gas evolution so that there may be no contradiction between the two results. Berndt's studies were done with flashlight battery plates, which probably contained no expander and therefore had relatively poor low temperature negative plate performance. Furthermore a battery designed for operation at -10°C using Berndt's plates would show little further deterioration of negative plate charge acceptance but substantial deterioration of positive plate performance. This is due to the fact that, at a reasonable charging current density (say 20 mA/cm^2), most of the deterioration in charging efficiency has already taken place when the negative plate temperature decreases to -10°C whereas the deterioration is only beginning when the positive plate reaches that temperature.

In a similar study of charge acceptance efficiency (8) at somewhat higher temperatures (0 to 40°C), in which the rate of both H_2 and O_2 gas evolution were measured, recharge was continued until the motorcycle batteries being used reached full charge. Positive plate efficiencies became progressively poorer in comparison to negative plate efficiencies as the batteries became more fully charged. At 0°C , after the return of 7 Ah and 10 Ah (to a 12 Ah battery, previously discharged by 10 Ah) the positive recharge efficiencies were 63.4 and 34.2% respectively whereas the negative efficiencies were 98.9 and 70.0% at the 0.8C rate of charge. It was suggested that the charge acceptance of the positive plate was influenced by the production and subsequent decomposition of persulphuric acid.

There is good evidence (35) from discharge characteristics of battery plates that, for a battery fully charged at room temperature, the negative plates lose recoverable capacity much more rapidly than the positive plates as the discharge current increases and as temperature decreases. From the functional relationships between capacities, current densities and discharge times and the discharge parameters determined (34), it is possible to derive an equation to optimize discharge capacity at a desired temperature by varying the relative areas of positive and negative plates. Thus for the plates tested, the capacities ($A \text{ min/cm}^2$) of the negative and positive plates respectively were given by

$$C_- = 0.32 (1 + 0.021T)/I^{0.4} \quad [1]$$

$$C_+ = 0.24 (1 + 0.015T)/I^{0.4} \quad [2]$$

where I is the discharge current density (A/cm^2).

These will be equal at $T = -26^\circ\text{C}$. Therefore at $T < -26^\circ\text{C}$ a larger negative plate area would be required to equal the positive plate capacity. If the negative and positive plate current densities are defined by $I_- = i/A_-$ and $I_+ = i/A_+$ for discharge current i , the optimum ratio of negative to positive plate area A_-/A_+ for any temperature T can be calculated from

$$\left(\frac{A_-}{A_+}\right)^{0.4} = 0.75 \frac{(1 + 0.015T)}{(1 + 0.021T)} \quad [3]$$

Hence $A_-/A_+ = 1.83$ at -40°C or 0.75 at 0°C .

Further studies of the effect of temperature and current density on the utilization of lead acid plates (13) also indicated that positive plate utilization was limited at low temperatures and high discharge current densities but that, in addition, negative plate utilization was limited due to coverage of active material by PbSO_4 .

Both these studies are related to limitations of the discharge rate, not of the charge acceptance rate and as the above calculations suggest, can be obviated by design considerations of optimum negative to positive plate ratios.

On the basis of the limited amount of work that had been published, it appeared that the positive electrode temperature dependence should receive the most attention and that an intensive research study of its mechanism at normal and at low temperatures was warranted. Electrochemical studies on pure lead electrodes were carried out at DREO and were supplemented

by electrochemical and physicochemical contracted studies at Cominco and at Gould, which will be discussed.

Although the negative electrode was judged to be of secondary importance, there was considerable work done on it at Cominco and some at DREO. Cominco compared the results for pure lead as a substrate for both negative and positive electrochemically formed electrodes with similar studies on antimonial lead alloys and on alloys containing calcium and tin.

The results and interpretation of all the research will now be discussed, followed by conclusions and recommendations for further work.

RESEARCH ADVANCES (1974 TO MAY 1977)

Discussion of the research carried out within the current program will be facilitated by dividing it into the two categories used in the previous section: firstly into studies related to specific components of the battery and secondly into studies of the battery system as a whole (black box).

STUDIES OF BATTERY COMPONENTS

POSITIVE ELECTRODE STUDIES

Since the positive electrode seemed most likely to be the limiting component, based on previous work, it was studied more thoroughly than were the other components.

Electrochemical techniques were applied to the study of electrochemically formed $\text{PbSO}_4/\text{PbO}_2$ electrodes in sulphuric acid at temperatures from 0°C to -50°C (36). Anodic oxidation peaks in the cyclic voltammograms were observed at lower positive potentials than the apparently corresponding reduction peaks at moderately cold ($\sim 0^\circ\text{C}$) temperatures. This seemed impossible unless the electrode interior during oxidation (charging) was less acidic than during the reduction (discharge). Although it later became apparent (37) that there was an additional oxidation peak and reduction plateau to explain the originally observed phenomenon, the conclusion of a more alkaline electrode interior remained valid. During constant potential oxidation of such a deeply discharged anodic film, a quantitative fit of a model of charging current, limited by a nucleation and growth process, preceded and followed by diffusion processes within the pores, was obtained (36,38) at all temperatures in the range 25°C to -50°C . The observed lack of dependence of charging current on electrode rotation rates (at 400 rpm to 3600 rpm) during most of the charging period, clearly indicated that the

diffusion-limited processes were occurring within the electrode pores and not in the bulk of the electrolyte. This conclusion was supported by interferometric studies of a lead acid cell, funded by a DRB grant (23). At low temperatures, further anomolous results were obtained in rotating ring disc electrode (RRDE) studies designed to detect soluble reaction intermediates. Because of inadequate instrumentation, the currents measured were very noisy and no conclusions could be reached. A double potentiostat has just been received for further experimental RRDE work.

When the temperature dependence of the rate laws for diffusion were quantitatively analyzed (39) it was found that diffusion coefficients and activation energies (up to 23 kcal mol^{-1}) were of the wrong order of magnitude for diffusion in solution. The cyclic voltammetry results also indicated a charging process with an activation energy $\geq 13 \text{ kcal mol}^{-1}$ (21f, 37). Based on the model for room temperature oxidation, previously developed (38), it was concluded (39) that pore blockage, and depletion of reactant species in the limited free space in the pores, occurred at low temperatures, before the electrode was fully recharged. The blockage appeared to be due to the formation of ice in the slightly alkaline pore-electrolyte, although some other mode of pore restriction was possible, such as persulphate adsorption or the formation of $\alpha\text{-PbO}_2$ from PbO (positive volume of reaction). This last possibility is consistent with observations of the effect of phosphoric acid on low temperature charge acceptance, which will be discussed later.

The conclusions reached above were based on studies of electrodes formed on pure lead substrates (36,38,39,22a-22d,22f). However it was shown in further cyclic voltammetry work that the major oxidation and reduction processes, at potentials relevant to positive plate conditions for a lead alloy containing 3.4% antimony (a normal battery grid alloy), showed no significant qualitative differences compared to pure lead (22e,22g,37) although negative electrode processes and positive charging efficiency were affected. Similar conclusions with respect to positive electrode behaviour, were reached (22h) for Pb-Ca and Pb-Ca-Sn alloys which are used in "maintenance-free" batteries.

It was confirmed that the low charge acceptance of the positive electrode at -40°C was indeed very low (21f) and an unusual energy storage-release phenomenon, related to state of charge (charge level) and terminal discharge potential, was observed (21m), which may be related to a dischargeable solution species, as previously suggested (6). The significantly higher (though less reproducible) charging efficiency obtained (21m) for antimonial lead in comparison with pure lead, suggested that efficiency might be improved by the action of an added metal ion, a suggestion which was pursued with positive results, in a study of the effect of electrolyte additives, to be discussed in a later section. Confirmation that certain metal ions, when added to a pasted plate, improved the positive electrode charge acceptance at -40°C will be discussed in the same later section.

Confirmation of the conclusions drawn from purely electrochemical studies were sought by means of physico-chemical measurements. Although these are still incomplete, the following results have been reported: the lowering of temperature to -40° resulted in a reduction of PbSO_4 crystal size from ~ 2 to $3 \mu\text{m}$ to ~ 0.5 to $1 \mu\text{m}$ and an elongation in shape. Identification

of material of submicron dimensions, believed to be PbO_2 on the lead sulphate crystal faces, was beyond the resolution of the SEM (scanning electron microscope) (21b,21f). X-ray diffraction measurements (21d,21f) confirmed smaller particle size and indicated that $\beta\text{-PbO}_2$ was discharged in preference to $\alpha\text{-PbO}_2$ at room temperature. This is in agreement with recent work, on pasted plates containing mixtures of α - and $\beta\text{-PbO}_2$, which showed equal participation of the two PbO_2 modifications in the discharge reaction at 45°C but preferential discharge of $\beta\text{-PbO}_2$ (and thus relative inhibition of $\alpha\text{-PbO}_2$ reduction) at lower temperatures or as the discharge current was increased. It was concluded (71) that positive active masses, rich in $\beta\text{-PbO}_2$, have a higher proportion of fine pores which block up relatively quickly during discharge. The X-ray diffraction studies (21d,21f) also indicated that the $\text{PbO}_2/\text{PbSO}_4$ ratio, while lower in films charged or discharged at -40° than at room temperature (21d, 21f) (as expected), was not necessarily correlated with charging efficiency (21m). Electron microprobe measurements (40) indicated that the sulphur concentration was highest at the surface but the resolution was insufficient to find significant differences between films formed at room temperature and at -40° (21f). In the earlier work (21f), the SEM technique seemed to be the most useful, and the most significant result reported above was the decrease of crystal size with temperature, which may be a factor in inhibition of nuclei formation at low temperatures. The electrochemical studies of nucleation (36) also indicated that the size of PbO_2 nuclei formed decreased with temperature.

Difficulties were encountered in the preparation and examination of samples of electrochemically formed films using the electron microprobe and X-ray diffraction techniques. These difficulties are not expected to be as great when studying battery plates. Work will continue under a new contract (60) to solve the difficulties in order to obtain further direct evidence in support of the electrochemically-based inferences (41). Further conclusions related to positive plate charging will be discussed in a later section (on electrolyte and plate additives).

NEGATIVE ELECTRODE STUDIES

Although studied in less detail, a number of interesting and potentially useful results arose from the negative electrode studies, carried out chiefly by Cominco (21,22,37) but at DREO as well (37). The cyclic voltammetry in the region of the negative plate potential was extremely complicated. This was particularly true at low scan rates and temperatures (37) for pure lead, and for lead-calcium alloys if cycling was carried out over a range of potentials, including those more positive than the Pb/PbSO_4 potential by 600 mV or more depending on scan rate. Some portions of the voltammograms were also dependent on electrode rotation in such a way as to indicate a limiting role by bulk electrolyte diffusion. Even further complications arose for antimonial lead (37), including a lowering of the hydrogen overpotential by about 0.4V compared to pure lead. Although the hydrogen overpotential was not very sensitive to temperature, the PbSO_4 reduction (charging) peak shifted to more negative potentials as temperature decreased so that the current rises for both processes overlapped at -40°C (22g,21f). This suggests that for well-cycled antimonial grid batteries, where time-dependent antimony

contamination of the surface of negative plates may occur, the recharging of the battery could eventually become limited by the negative plate, even if initially limited by the positive (22g).

On the other hand, the addition of calcium to lead seemed to facilitate the reduction of PbSO_4 to metallic lead, especially at -40°C (22h) but the addition of tin reduced the hydrogen overvoltage by about 0.2V compared to pure lead. (More recent work at DREO of hydrogen evolution on electropolished electrodes calls this latter finding into question.) "Maintenance free" SLI batteries typically contain grid alloys of 0.6% Sn and 0.06% Ca, with the tin added to increase castability and reduce corrosion. Lead-calcium alloys without tin have long been used in batteries on full-float service in telephone systems. Some batteries containing calcium grids and hybrid antimonial and calcium grid systems are being evaluated for low temperature performance in a current DREO evaluation program (26). More quantitative low temperature and room temperature hydrogen evolution studies on lead and lead alloys are also in progress at DREO to study the effect of alloying metal more carefully.

Other aspects related to negative plate characteristics arose from the full battery studies and will be discussed in a separate section.

EFFECTS OF ELECTROLYTE COMPOSITION

An early effort was made to increase the pH of the solution without increasing the freezing point excessively and thereby favour the formation of PbO_2 relative to O_2 at the positive electrode and the formation of Pb relative to hydrogen at the negative electrode. Solutions of aqueous sulphuric acid, ammonium sulphate and alcohol mixtures were evaluated in terms of positive electrode charge acceptance (33) at room temperature. Encouraging results were obtained in the room temperature half cell studies cited but solutions near the optimum composition did not result in significantly improved low temperature charge acceptance in commercial batteries.

An intensive study was made of the temperature dependence of lead sulphate solubility in sulphuric acid solutions (34) both at DREO and at Cominco. The information obtained was relevant to previous theoretical work (38,39) and was required to try to clarify the role of dissolved lead in the low temperature electrode kinetics (1,2,13,42). The results of this work showed that while thermodynamically predicted solubilities were eventually established at each temperature, equilibration was a very lengthy process. Days or weeks, depending on agitation and other experimental conditions, were required to reduce solutions supersaturated with lead to their saturation values in solutions with small excesses of lead sulphate. Thus states of supersaturation with respect to lead might easily be maintained for very long periods of time in a battery at low temperatures, unless the battery plates acted as much better nucleation centres than the fine crystalline lead sulphate precipitates present in the DREO solubility studies. It was concluded that the kinetics of dissolution were probably of more importance than the thermodynamics (34).

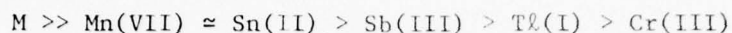
ELECTROLYTE AND PLATE ADDITIVES

Gould (20b) studied the effects of additions of phosphoric acid, nickel sulphate and cobalt sulphate to the acid in commercial batteries. Although all three reduced the charge voltage at -25°F , the sulphates slightly increased capacity but did not improve charge efficiency and the phosphoric acid had a detrimental effect on low temperature capacity. Elsewhere, phosphoric acid has been found to have a beneficial effect on corrosion and cycle life (43-45) but to cause excessive mousing (59) and to be detrimental to high rate and cold performance (45,59). Increased cycle life is apparently related to increased $\alpha\text{-PbO}_2$ content in positive plates whereas electrochemical capacity may be related to $\beta\text{-PbO}_2$ content (46). Thus $\alpha\text{-PbO}_2$ formation, which appears to be facilitated by the presence of small amounts of H_3PO_4 (47), could be a cause of poor low temperature performance by contributing to a loss of plate porosity during charging at low temperatures. Alternatively, $\alpha\text{-PbO}_2$ is inhibited at low temperatures (71); accordingly the relatively small amount of $\beta\text{-PbO}_2$, which is discharged, may passivate quickly at high rates due to blockage of its relatively fine pores. Such blockage may be due to freezing or to some other mechanism.

As previously mentioned, the beneficial effects of antimony on charge acceptance (21h,21m) suggested that the efficiency might be improved by metal ion additives. It was proposed (21m) that the effect of antimony on charge efficiency is a catalytic one, although Ruetschi and Angstadt proposed (48) that Sb gives rise to holes and pores in the PbSO_4 layer. Panesar (49) disagreed with the latter explanation, but his arguments were based on an assignment of the cathodic peak near -800 mV (relative to $\text{Hg}/\text{Hg}_2\text{SO}_4$) to $\alpha\text{-PbO}_2$ reduction, which is probably erroneous. The postulate that antimony increases positive plate porosity may still remain tenable but in view of the finding that antimony gives rise to increased $\alpha\text{-PbO}_2$ content in the formed active material (50), some inconsistencies between the relationship of $\alpha\text{-PbO}_2$ to plate porosity and to the presence of Sb and H_3PO_4 obviously remain to be resolved. Perhaps temperature is an additional independent parameter or porosity and $\alpha\text{-PbO}_2$ content are not directly related. A key to the resolution of this problem may exist in more recent work by Burbank (72), who found that cycling of antimonial lead increased the amount and crystallinity of $\beta\text{-PbO}_2$ gradually in comparison to pure lead. A corrosion layer of $\alpha\text{-PbO}_2$ was attached to the metal in both cases. It was concluded that antimony acted as a nucleating catalyst for $\beta\text{-PbO}_2$ in the corrosion layer and promoted intercrystal bonding between the two PbO_2 polymorphs.

The effects of thirteen soluble electrolyte additives and one lead substrate additive (Sb) were tested on electrochemically formed films (21i, 21j). Additions of a few hundred ppm were made both at -40° and during film formation at room temperature. When added at -40° only one of the additives (designated here as M to prevent premature disclosure, pending the completion of patent procedures, but disclosed in restricted reference 21n) produced a definite positive effect (21m) and three (Co, P and Th) gave decidedly negative effects. For additions during film formation at room temperature, the low temperature charge efficiency was increased by the following six

elements in order of decreasing effectiveness.



Further studies of element M at 190 ppm indicated a 70-fold improvement factor (2lm). The additive appeared to deposit on the positive electrode (as was confirmed by AA analysis) and its beneficial effect was retained when the electrolyte containing the additive was removed and replaced by pure acid solution.

For films formed on antimonial lead (2lh,2lm) and for films formed in the presence of additive M (2lj,2lm), the capacity increased more slowly with cycling than for pure lead in pure electrolyte. Furthermore the capacity per unit weight of film was lower than for pure lead, indicating that Sb and M had entered the film. The improvement factor more than compensated for the increase in weight for films of similar capacity (2lm). Scanning electron micrographs were taken of the film in the discharged state (2li,2lj) but there appeared to be no correlation between morphology and the charge acceptance results.

There was some evidence from open circuit decay phenomena observed during thin film half-cell studies (2lj,2lm) that the presence of M in the electrolyte may be incompatible with proper functioning of the negative electrode. Accordingly, tests of M as well as Mn(VII) and Sn(II) as electrolyte additives were carried out in commercial 6 Ah motorcycle batteries (2ln). Mn(VII), added as KMnO_4 , had a small negative effect on charge acceptance efficiency (unlike its effect on thin films) and Sn had a slight positive effect even at low charging rates. The addition of 1000 ppm of M to the electrolyte of a battery had no appreciable effect on -40°C charge acceptance. At 3200 ppm or more, massive deposits of M formed on the negative plates and cell potentials fell to as low as 1.6V. The direct addition of either M or Sn to a battery after manufacture was thus found to be inefficient, due to extensive reaction with the large active surface of the negative electrode, where these elements are precipitated.

Tests were carried out in cells made up of a single pasted positive electrode between two lead sheet electrodes in a large excess of acid. Additive M was added in two ways: via the electrolyte by continuous addition during formation of the positive, or directly to the leady oxide of the paste. Although there was no appreciable improvement in -40°C charge acceptance at low rates, a slight improvement was obtained at the 1.25-hour rate and an improvement by a factor of almost 2 was obtained for immediate recharge at the 45 minute rate, for electrodes for which M was added to the paste. The relative improvement seemed to be due to a reduction in charging efficiency of the untreated plates to about 30% when the charge rate was doubled whereas the efficiency for the treated plates remained at about 50 to 65%, which is more characteristic of 1 to 3 hour charge rates.

Further work is planned under contract (60) to investigate the preferred mode of addition of M to the positive electrode, its optimum concentration and its effects on negative electrode performance and battery cycle life. Patent applications are being processed. As yet unexamined additives and additive combinations, will also be screened using thin film

positive electrodes.

It is noteworthy that, in comparative studies of batteries made with antimonial lead grids and with lead-calcium-tin grids, Gould reported (20d) relatively good low temperature charge acceptance for the latter. For approximately the same amount of paste, antimonial cells yielded only 27% of their room temperature capacity at -25°F following a low rate charge (C/20 to C/15), with 33% overcharge, whereas the corresponding value for lead-calcium-tin cells was 61%. At -35°F the capacities were 24% and 58% of room temperature values respectively. However the room temperature capacities for the antimonial cells were higher than for Pb-Ca-Sn, for the same paste weight. These findings may be related to Cominco's observation that film weight per unit of electrical capacity was increased when Sb or M had been added to the pure lead positive electrode thus reducing room temperature capacity but improving low temperature charge acceptance (21m). Charge acceptance efficiencies were also less for antimonial than for calcium-tin lead alloy batteries at low temperatures. Gould's finding (20d) that the room temperature capacities of lead-calcium-tin cells decreased on cycling must be qualified. The deep discharges that Gould used to measure recoverable capacity would have been expected to cause earlier failure and loss of capacity for lead-calcium-tin cells than for antimonial cells since the former are more susceptible to failure on deep cycling (51,69).

The flatter capacity-temperature relationship for lead-calcium-tin cells suggest that tin (or possibly calcium) additions to the active material could also be made via the grid or substrate, as was found for Sb in the Cominco work. Batteries with lead-calcium-tin grids for both positive and negative plates as well as hybrid batteries with calcium-tin negative grids and antimonial positive grids are currently being evaluated at DREO (26). The presence of antimony in the positive plate might be expected to improve its charge acceptance whereas its absence in the negative grid might increase hydrogen overpotential until the antimony corroding from the positive plate deposits at the negative and lowers hydrogen overpotential. If this occurs the performance of the hybrid battery might be expected to deteriorate during shallow charge-discharge cycling faster than the antimony-free battery. An evaluation of the opposite hybrid might be carried out later if considered worthwhile.

Carbon has also been studied as a positive plate addition agent. Preliminary results (20b) suggested that 0.2 to 0.4% carbon might be beneficial to positive electrode charge acceptance. The earlier results were not reproducible (20c,20d) however, even though several types of carbon were tested (20d). Even when small beneficial effects were obtained, they did not persist after a few charge-discharge cycles.

STUDIES OF THE COMPLETE BATTERY

BATTERY HEATING

Techniques and devices for increasing the internal battery temperature by various heating methods have already been discussed. The device judged quickest, most efficient and most promising was a magnetic induction heater produced by VARTA AG. Life cycling tests will be carried out at DREO (52) to determine the effects of magnetic induction heating on battery cycle life. The cycling test is based on Life Test SAE J240a (53) but with alternate weeks at the +40°C test specification temperature and at -40°C and with further modifications to allow for battery size and for the lower capacities during the low temperature interval. Although failure during the SAE J240a test may occur by different failure modes than in real automotive service, the prime objective of the study is to confirm the value of the magnetic induction heater and to look for possible detrimental effects.

CHARGING METHODS

The effect of pulse charging on charge acceptance efficiency of electrochemically formed positive films was investigated by Cominco (21e) over a wide range of conditions, including sine, square and triangular wave forms of various amplitudes, frequencies (10-1920 Hz) and symmetries. Comparison with smooth charging at the same average currents showed no effect, but some work on thicker films was suggested because the benefits of pulse charging could not be completely discounted.

At Gould the effect of square wave (120 Hz and 2000 Hz) pulse charging on batteries containing PVC separators was studied (20b) at -25°F. Symmetry and d.c. offset were varied and it was found that a small improvement in charging efficiency, in comparison to a steady current of the same average value, was observed when the pulse duration was very short (50 μ s) and the rest period between pulses at least 10 times longer than the pulse duration. No estimate of reproducibility was given to determine whether the improvement (of $\sim 10\%$) was significant.

PRIOR DISCHARGE

Although perhaps of limited practical application, it was found (20b) that an immediately prior discharge improved battery charge acceptance substantially due to internal heating during the discharge. Only one discharge-current was reported (25A for 1 hour from an 80 Ah battery - this was termed a "low rate" discharge, presumably relative to cranking rates).

A decrease of temperature was observed during an immediately subsequent recharge, compared to an increase of temperature during recharge following an overnight stand. This may have been due to release of latent heat of fusion during the discharge due to freezing of diluted electrolyte in the pores. During the immediately subsequent charge, cooling may be due to thawing (absorption of latent heat of fusion) or to heat dissipation down thermal gradients established in the battery during the discharge. Independent observations (25) suggest that the beneficial effect should be even more pronounced with higher discharge currents, when both the latent heat and ohmic heat released within the battery prevent excessive pore electrolyte freezing and produce an increase of internal temperature. This effect should be greater at high rates when thermal dissipation is slow relative to the rate of production.

DREO MODERN LEAD ACID EVALUATION

During the course of the work described above, it became apparent that a number of possible approaches to improving low temperature charge acceptance and performance might already have been incorporated into some of the newer modern lead acid batteries which have recently appeared on the market, or will be available soon.

One approach to improved low temperature capacity and charge acceptance is an increase of active plate surface area per unit weight or volume, by the use of thinner plates. This would not have been feasible with traditional Pb-6% Sb grid alloy batteries due to the excessively high rate of self discharge of antimonial batteries at normal temperatures. This is not so serious a problem in non-antimonial cells made with lead-calcium-tin grids, such as those in maintenance-free batteries, and is even less serious for currently available sealed cells with almost pure lead electrodes.

Maintenance-free batteries made by Delco and by Gould were therefore acquired for testing in the DREO evaluation task (26). Hybrid batteries made by Gould containing antimonial positive plates and lead-calcium-tin negative plates were also obtained for comparison, to obtain an indication as to whether antimony migration across the cell and consequent negative plate discharge, was more or less important than positive plate corrosion alone in causing self-discharge, and whether antimony migration and deposition might lead to increased hydrogen evolution at the negatives.

Batteries made by Yuasa with thin (0.1 to 0.2 mm) microporous Yumicron^R separators, lined with (≤ 0.5 mm) glassmats, claimed to be impermeable to antimony, are also being evaluated. The antimony impermeability was claimed to have been measured directly although no references are given (54). If substantiated, such a separator, which is microporous PVC with fibres of polyester or polypropylene as base material (70), could be used in a cell with antimonial positive plates to prevent the lowering of hydrogen overpotential at the negative caused by antimony deposition. However the Yuasa batteries are also being evaluated because the thinner separator is claimed to have a lower electrical resistance ($3 \times 10^{-4} \Omega/\text{dm}^2/\text{sheet}$) than conventional separators and would permit the incorporation of additional active

material into the space saved by using the thinner separators (54). Higher energy densities, particularly at high cranking rates, are therefore to be expected both because of increased capacity and higher discharge voltages.

Sealed lead-acid cells (55,56) produced by Gates Energy Products Inc. (and by General Electric, under Gates' licence) have been shown to have exceptional low temperature performance, lifetime (200 deep (100%) discharges, over 2000 moderate (30%) discharges) and wet storage characteristics (3 years at 25°C) (55-59). The Gates cells contain phosphoric acid as an additive to improve positive electrode performance and have extraordinarily high surface area electrodes because of their unique "jelly-roll" spirally-wound construction. Separator resistance is low and since no antimony is present, self discharge is sufficiently slow (58) to permit very high area plates and therefore high discharge rates. The largest cells currently produced are 25 Ah "#6" cells (B.C. for Beer Can cells) and cells are priced to compete with sealed Ni-Cd (\$4 D cell). Although they are still relatively expensive, evaluation is being carried out to determine whether the cells' features promote low temperature charge acceptance sufficiently to justify developing the principle of thin plate, antimony-free construction for batteries designed for cranking applications. It is likely that much smaller battery capacities could be used with the sealed system (unless requirements for power for other than cranking purposes were of over-riding importance) because of the cells capability for much higher discharge rates than normal, eg. 40% of rated cell capacity at the 15C rate (55).

In addition to attempting to confirm that features which are already present in existing commercial batteries will promote low temperature charge acceptance, as well as good discharge characteristics, the lead acid evaluation program in progress should lead to the development of low temperature test procedures and upgrading of specifications for CF batteries.

FURTHER DISCUSSION, CONCLUSIONS AND RESEARCH RECOMMENDATIONS

The positive $\text{PbSO}_4/\text{PbO}_2$ electrode has received the most attention during the current investigation because it has appeared, on the basis of previous work, to be the cell component most likely to limit low temperature charge acceptance. A model for positive electrode charging was developed (38,39), based on results with pure lead electrodes, which suggested that pore blockage due to electrolyte freezing or some other mechanism, eventually prevented positive electrode charge acceptance at very low temperatures. Since the model for low temperatures was drawn by inference from electrochemical measurements and was supported by direct physico-chemical evidence only for more normal temperatures, further electron-optical work is required for direct confirmation (60).

Additional electrochemical studies would also be useful in refining the model further. Linear scan voltammetry and potentiostatic transient methods were applied to obtain quantitative kinetic information about electrode charging. The electrodes were discharged fairly deeply in both cases before recharging. Further LSV data, following a discharge at ~ 100 mV cathodic to the $\text{PbSO}_4/\text{PbO}_2$ potential, would be useful in order to aid the analysis of the previously acquired data, for which discharge was at 0.6V (to 0.6 μA) i.e. ~ 500 mV cathodic overpotential. This additional data would help to interpret the relative contributions to the observed currents due to $\alpha\text{-PbO}_2$ and $\beta\text{-PbO}_2$ formation, which may be highly relevant to low temperature charge acceptance.

Faradaic impedance methods were also employed in the DREO study (36) to obtain the resistive and capacitive components of ac during charge and discharge. The data thus obtained was limited, however, and was used only in a semi-quantitative way, to interpret the progressive changes of PbSO_4 resistance and PbO_2 surface area during the course of their consumption or formation. Although differential capacitance and electrode resistance measurements have been made on α - and $\beta\text{-PbO}_2$ (61,62), a detailed study, in which both ac components were measured on a $\text{PbSO}_4/\text{PbO}_2$ electrode as a function of imposed potential and over a wide range of frequencies, is needed. An effort could thus be made to fit a detailed analogue circuit model of an electrode with time-dependent ac components, due to the changes in PbSO_4 and PbO_2 content and configuration.

Rotating disc (RDE) and rotating ring disc electrode (RRDE) methods were used at DREO in an attempt to study diffusion and to detect long-lived soluble intermediates, which upon formation at the disc, could be detected by capture at the insulated and electrically separate surrounding ring. Although no dependence of disc oxidation currents on rotation rate was detected between 400 and 3600 r.p.m., near the $\text{PbSO}_4/\text{PbO}_2$ potential, an anomalous inverse dependence was observed between 0 and 400 r.p.m. (36) i.e. the current was higher for a stationary electrode than for a rotating one: in contradiction to what would be expected if diffusion in solution was current-limiting. Clear, distinct, but complicated reduction current peaks were detected at the ring of the RRDE as the potential of the disc was scanned cathodically through the PbO_2 reduction peak (December 1974). Ring reduction currents were also observed during the cathodic scans at more positive potentials. However ring potentials were sometimes difficult to maintain, ring currents, apparently in the wrong direction (as in the case cited above unless tetravalent lead or some other oxidized species was released during reduction of the PbO_2), were often observed and excessive noise was a problem. If the ring reduction current during disc reduction was not spurious, it was probably related to loss of active material during rotation, which would explain the inverse rotation dependence observed in 0-400 rpm range. However, since the results may have been spurious, due to an undesirable interaction between the potential-controlling circuits for the disc and the ring, confirmation and more quantitative further study is required, using a double potentiostat recently acquired.

Potentiostatic positive electrode oxidation transients were followed for only a limited time to ensure quantitatively reproducible data (36,38,39). Some further studies, including physico-chemical measurements, of electrodes polarized for longer times following the minimum in the current (after the nucleation and growth peak) would be of use. In this way, the changes in the

electrode during the subsequent current increase at normal temperatures (the current did not increase at low temperatures and normal charging potentials) would further elucidate the mechanisms of low temperature charge blockage.

One puzzling experimental phenomenon, which unfortunately was not pursued, was the observation that the current, during discharge of the positive electrode at high constant overpotentials (200-600 mV), was very precisely inversely proportional to time over a range of several orders of magnitude in time and current. No model was ever found or developed to explain this relationship.

Further open-circuit decay measurements for both positive and negative electrodes at -40°C and at room temperature would clarify previous results. Potential arrests frequently occurred at potentials corresponding to processes, which have not been clearly established. Plateaux have been observed at -40°C at potentials other than and in addition to those reported by others at higher temperatures (63,64,65). Open circuit decays, which are much slower at -40°C , might be coupled with suitable analytical or electron-optical methods to study the potential determining couple at such arrests or plateaux.

The processes occurring at the negative electrode, although less pressing from a practical point of view, are nonetheless no better understood. Once the low temperature charge acceptance is sufficiently improved by modifications to the positive plate (see below) it is likely that the negative plate will become limiting. To some extent this can probably be overcome for practical purposes by increasing the negative area as discussed (not a feasible approach for positive antimonial plates) or by expander purification. However, such measures may not be adequate. Furthermore during the earlier stages of charging, the charging current does appear to be limited by the negative plate. Thus further research into the mechanisms of negative electrode charging reactions are required. Some hydrogen evolution studies on lead alloys are currently in progress. These should be continued, including a study of the hydrogen equilibrium which appears to take place under a lead sulphate film, when Pb electrodes in sulphuric acid reach an open circuit potential of about +350 mV relative to the Pb/PbSO₄ potential (4). Although negative plates are rarely discharged that deeply, an understanding of the electrode structure corresponding to such a potential arrest would be useful and would contribute to an understanding of the processes of plate formation.

Other negative electrode studies could be carried out using the same electrochemical and physico-chemical methods as for positive electrode studies. It would be particularly interesting to be able to explain the complicated voltammetric pattern (37) observed during reduction of an anodically formed film, which is usually considered to contain only PbSO₄, but must contain other divalent lead compounds as well.

Certain electrolyte additives produced beneficial effects on low temperature positive electrode recharge and action has been taken by D Pat A (Wayne Anderson) to protect the patent rights of the crown. Further work is in progress (60) to evaluate other additives suggested by the previous work, and to evaluate combinations of the most promising ones for possible synergistic effects. Additions to the electrolyte resulted in the beneficial agents being

taken up and retained by the positive electrode but with simultaneous deposition, and consequent detrimental effects, on the negative plates in commercial cells. However certain of the same additives also gave beneficial effects when added directly to the active electrode material before pasting. Further work is in progress (60) to investigate the mode of addition (via electrolyte, paste or grid) and relative effectiveness of the additives and their side-effects on battery and negative plate performance, in terms of cycle life, temperature dependence, cell potential, etc. To distinguish between electrolyte additives which remain in the electrolyte and those that are taken up by the active material, the term "modifier" is now being used for the latter (60). Work is also required to determine under what conditions the positive electrode or negative limits the charge acceptance, particularly in cells containing modifiers. Some studies along these lines are planned as are electron-optical studies to try to determine the effects of the modifiers on electrode properties (60). Electron-optical studies of anodic films on pure lead are planned to attempt to verify the models developed. This work should probably be expanded to include X-ray, porosimetry and other appropriate methods to determine α/β PbO_2 ratios and basic sulphate contents of battery plates, formed under various conditions of temperature and cycling, and with or without the modifiers found to benefit low temperature charge acceptance. As previously discussed, the relationship between antimony, phosphoric acid, α/β PbO_2 ratio and porosity required clarification. Very recent work (67), part of a study on battery paste reactions (68), indicates that X-ray diffractometry can be used to quantitatively determine tetragonal PbO and tri-basic and tetrabasic lead sulphate contents in quaternary mixtures also containing orthorhombic PbO , using a cold mounting resin technique. $\text{PbO}(0)$ can also be determined provided that its particle size is within an acceptable range. Perhaps an even more powerful tool, though less quantitative, is an unreported technique (73), which involves the use of polarized light for sample illumination, developed at Globe-Union. Metallographic grid sections, including active material, are mounted by a vacuum impregnation method and microphotographs are taken using reflected polarized light. By suitable choice of polarizing angles α - PbO_2 , β - PbO_2 , PbO and PbSO_4 appear as coloured phases, which can clearly be distinguished. Chemical and physical analyses were used to correlate the colours with composition and morphology. Results, obtained at normal room temperatures, were in agreement with the DREO electrode modelling (38). Such a technique could be directly extended to studies of temperature effects on the morphology of pasted plates.

Some solubility studies to determine lead sulphate dissolution kinetics in real batteries would be useful, particularly if separate catholyte and anolyte analyses could be made.

New grid alloy compositions are actively being developed and tested by the industry to find alloys which combine the favorable properties of antimonial and calcium-tin-lead alloys without their disadvantages. As batteries containing these alloys become available, they should be tested for low temperature charge performance as part of an ongoing modern lead acid battery evaluation program. New plastic separators such as PVC, polyethylene, polypropylene, etc. are also being introduced into modern batteries and this may necessitate testing for low temperature charge efficiencies. For example Yuasa's Yumicron separators, in addition to their thinness, low resistance and chemical stability, are claimed to be impermeable to antimony. This may be an important characteristic in maintaining high negative plate hydrogen

overpotentials and thus retaining negative plate chargeability at low temperatures. New electrolyte or paste formulations may contain additives such as phosphoric acid to promote desired battery characteristics for particular alloy compositions. Since these may also be harmful to low temperature performance, testing may be required. Such testing is not normally done by the manufacturer in an standardized way and is needed if the CF are to have a standard basis of comparison of the newer batteries.

The required lines of development of the electrode modifiers being evaluated by Cominco (60) can be anticipated to some extent. Thus an optimization phase, following or in parallel to the current research work, using a commercial manufacturing process, is a logical next step. The details of optimization parameters, anticipated benefits, justifiable funding, likely exploitation etc., remain to be worked out. Some will follow directly and naturally from the current work but it is premature to recommend a specific development program in the present report.

The research results which were negative or inconclusive, such as pulse charging, certain electrolyte or plate additives etc. have been discussed earlier in the report, and will not be repeated here since the purpose of this section is to indicate the direction of future work.

In sum, a great deal has been learned about the lead acid battery, both at normal and at low temperatures, during the last few years, and a significant contribution to knowledge in this field has been made. Although progress has been substantial, answers to many questions are still needed before a clear understanding of the battery mechanisms will be possible. However, there are encouraging signs of inexpensive methods of obtaining practical improvements to low temperature performance. Some of these require further exploration and others have already been built into available commercial batteries.

REFERENCES

1. Final Research Reports. "Development of Effective Means of Low Temperature Charging of Lead-Acid Batteries". Gould-National Batteries Inc., Research Laboratories, Depew, N.Y. U.S. Signal Corps Proj. No. 31-2023A: (a) Dept. of Army Proj. No. 3-91-02804, Contract No. W36-039-sc-38233, June 1951. (b) Dept. of Army Proj. No. 3-18-03-031, Contract No. DA-36-039-sc-5434, June 1952.
2. E. Willihnganz, "Power Sources 5", ed.-D.H. Collins, p. 43, Academic Press, London and New York (1975).
3. K.N. Campney, DRB Tech. Memo. No. 43, Defence Research Chemical Laboratories, Electrochemistry and Batteries Group, July (1960).

4. E.J. Casey and K.N. Campney, J. Electrochem. Soc. 102, 219 (1955).
5. T.E. King, E.J. Casey and I.H.S. Henderson, Proc. 16th Annual Power Sources Conf., May 22-24 (1962) p. 108, PSC Publications Committee, Red Bank, N.J.
6. I.H.S. Henderson, unpublished memorandum to E.J. Casey, DREO (1961).
7. C. Gardner and F. Rocheleau, DREO Technical Note No. 75-1, March (1975).
8. K. Peters, A.I. Harrison and W.H. Durant, "Power Sources 2, 1968", p. 1, ed.-D.H. Collins, Pergamon Press, London (1970).
9. S.O. Izidinov and É.Kh. Rakhmatullina, Soviet Electrochemistry 4, 575 (1968); Elektrokimiya 4, 647 (1968).
10. E.V. Kasatkin and A.A. Rakov, Electrochim. Acta 10, 131 (1968).
11. "Record of Lead-Acid Battery Seminar Held at DREO 5 December 1967", DREO Technical Note No. 69-18, November (1969): (a) K. Ekler, Paper No. 1; (b) C. Luciani, Paper No. 5.
12. D. Berndt, Chemie-Ing. Techn. 36, 627 (1966).
13. D. Berndt, "Power Sources 2, 1968", ed.-D.H. Collins, Pergamon Press, London (1970).
14. K. Ekler, DRB University Grantee's Report, Proj. No. D52-54-80-14, Grant No. 5480-14, October (1968).
15. P.E. Baikie, M.I. Gillibrand and K. Peters, Electrochim. Acta 17, 839 (1972).
16. Minutes of 23rd meeting of the Advisory Committee on Electrical Power Sources, Item 6.1, para 10, 29 May 1972.
17. C. Luciani, Letter to Chairman/SWG on Applied Research/AC(EPS), 10 July 1972.
18. Minutes of 24th meeting of the AC(EPS), Item 2.5, 5 January 1973.
19. DREO, EPS Division, Quarterly Progress Notes, 1 October 1973 - 31 December 1973, March (1974).
20. Gould Manufacturing of Canada Ltd.
Research Reports for work done under Contract No. 2SR3-0122:
 - a. April 5 (1974);
 - b. January 20 (1975).And by sub-contract to Cominco Ltd. under Contract No. 2SR5-0020, DSS File No. 13SR.7090344:
 - c. August 18 (1976);
 - d. February 24 (1977).

21. Cominco Product Research Centre, Sheridan Park, Quarterly Progress Reports for work done under DSS Contract No. 2SQ3-0491, DSS File No. SQ17090243 and 12SW7090243:
- a. First QR, March (1974);
 - b. Second QR, July (1974);
 - c. Third QR, September (1974);
 - d. Fourth QR, January (1975);
 - e. Fifth QR, April (1975);
 - f. Final Report March (1976).
- And for work done under DSS Contract No. 2SR5-0020, DSS File No. 13SR.7090344:
- g. First QR, June (1975);
 - h. Second QR, October (1975);
 - i. Third QR, January (1976);
 - j. Fourth QR, May (1976);
 - k. Fifth QR, August (1976);
 - l. Sixth QR, October (1976);
 - m. Final Report, February (1977);
 - n. Addendum to Final Report, March (1977). Restricted.
22. Cominco Product Research Centre, Sheridan Park, Research Reports:
- a. Report No. 1, "A Linear Sweep Voltammetry Study on Polycrystalline Lead in Sulphuric Acid at Room Temperature", July (1974);
 - b. Addendum to Report No. 1, November (1974);
 - c. Second Addendum to Report No. 1, October (1975);
 - d. Report No. 2, "A Linear Sweep Voltammetry Study on Polycrystalline Lead in Sulphuric Acid at -40°C", November (1974);
 - e. Report No. 3, "A LSV Study on Antimonial Lead in Sulphuric Acid at Toom Temperature", April (1975);
 - f. Report No. 4, "Effect of Temperature, Between 25° and -40°, on the Cyclic Voltammograms of Lead in Sulphuric Acid", April (1975);
 - g. Report No. 5, "A LSV Study of Antimonial Lead in Sulphuric Acid at Low Temperatures to -40°C", April (1975);
 - h. Report No. 6, "LSV on Lead-Calcium and Lead-Calcium-Tin Alloys in Sulphuric Acid at Room Temperature and at -40°C", October (1975).
23. R.N. O'Brien, J. Electrochem. Soc. 124, 96 (1977).
24. E. Valerioté, Chemistry in Canada 27(11), 11 (1975).

25. "Inductive Heating of Starter Batteries" (In German), Varta AG Hanover, Talk given to representatives of the German automobile industry, June 9 (1970). [No author indicated but probably D. Berndt or possibly H.S. Panesar were authors].
26. E.M.L. Valeriote, L.D. Gallop and R.W. Gorman, "Low Temperature Lead Acid Evaluation: Preliminary Results and Revised Procedures", DREO Technical Note in preparation.
27. P.S. Amber, "Internally Heated Storage Batteries", Detroit Arsenal Components Laboratories Division, Report No. 699, March (1951).
28. "Internal Storage Battery Heating Devices", Signal Corps Contract No. DA-36-039 SC 42592, Dept. of Army Proj. No. 3-18-03-031, Signal Corps Proj. No. 31-2023A, Third Quarterly Progress Report, to July 31 (1953).
29. Joseph Lucas (Batteries) Ltd., Report No. F50094, "Warming and Charging the UK6TN Battery in Sub-Zero Temperatures", September (1961).
30. R.P. Blake, DH/DRDS, CDLS London, CR 8/7, 18 May (1976).
31. F. Schreier, International Defence Review 3, 346 (1974).
32. G.W. Vinal, "Storage Batteries", 4th Edition, John Wiley & Sons Inc., N.Y. (1955).
33. E.M.L. Valeriote, L.D. Gallop and R.J. McMahon, DREO Technical Memorandum 11/75 (EPS), March (1975).
34. P.J. Aragon, E.M.L. Valeriote and L.D. Gallop, "The Application of DPASV to the Determination of the Low Temperature Solubility of Lead Sulphate in Sulphuric Acid Solutions", DREO Report No. 802, February 1978.
35. P.E. Baikie, M.I. Gillibrand and K. Peters, Electrochim. Acta 17, 839 (1972).
36. E.M.L. Valeriote and L.D. Gallop in "Power Sources 5", ed.-D.H. Collins, Academic Press, London (1975); Defence Research Establishment Ottawa, DREO Report No. 717 (May 1975).
37. T.G. Chang, M.M. Wright and E.M.L. Valeriote, "The Cyclic Voltammetry of Lead and Lead-Antimony Battery Grid Alloy in Aqueous Sulphuric Acid at 25°C to -40°C", Paper No. 7, Proc. 10th Intern. Power Sources Symp., Brighton, England, Sept. 13-16, 1976; DREO Report No. 753, February (1977).
38. E.M.L. Valeriote and L.D. Gallop, J. Electrochem. Soc. 124, 370 (1977).
39. E.M.L. Valeriote and L.D. Gallop, J. Electrochem. Soc. 124, 380 (1977).
40. J.K. Pryor, Ontario Research Foundation Report on Job No. 74274, March 25 (1975).
41. E.M.L. Valeriote, DREO Memorandum to File 5480-08-12, 26 November (1975).

42. P. Ruetschi, "Power Sources 5", Proc. of 9th Internat. Power Sources Symp., ed.-D.H. Collins, Intervention, p 71, Academic Press, London (1975).
43. H. Bode and E. Voss, Electrochem. Acta 6, 11 (1962).
44. S. Tudor, A. Weisstuch and S.H. Davang, Electrochem. Tech. 4, 406 (1966); 5, 21 (1967).
45. K. Peters, "Phosphoric Acid as a Battery Additive", Chloride Tech. Centre TM #44, Jan. 72; Issue No. AM.22, May (1972).
46. J. Burbank, A.C. Simon and E. Willihnganz, "The Lead-Acid Cell", Adv. in Electrochem. and Electrochem. Eng., Vol. 8, ed.-P. Delahay and C.W. Tobias, p 157, John Wiley & Sons Inc., N.Y. (1971).
47. W. Visscher, J. Power Sources 1, 257 (1976/77).
48. P. Ruetschi and R.T. Angstadt, J. Electrochem. Soc. 105, 555 (1958).
49. H.S. Panesar, "Power Sources 3", Proc. 7th Internat. Symp., ed.-D.H. Collins, p 79, Oriel Press Ltd., Newcastle upon Tyne (1971).
50. J. Burbank, J. Electrochem. Soc. 111, 1112 (1964).
51. D.H. McClelland, Gates Rubber Co., private communication.
52. E.M.L. Valeriote, Memorandum to File 5480-08-12, May (1977).
53. "The Storage Battery Manufacturing Industry 1973-1974 Year Book", p 77, Battery Council International, Burlingame, Calif. (1974).
54. "Yuasa Yumicron Batteries", Yuasa Battery Co. Ltd., Tokyo.
55. I. Harrison, Electrical Rev. 198 (21), 34, 28 May/4 June 1976.
56. E.F. Lindsley, Popular Science, p 46, November 1975.
57. Gates Energy Products Battery Application Manual, Gates Rubber Co. (1975).
58. K.R. Bullock and D.H. McClelland, J. Electrochem. Soc. 123, 327 (1976).
59. K.R. Bullock and D.H. McClelland, submitted to J. Electrochem. Soc.
60. "Investigation of the Effects of Battery Plate Modifiers on Low Temperature Performance", Continuation of work commenced under Contract 2SR5-0020, DSS File No. 13SR.3237010.
61. J.P. Carr, N.A. Hampson and R. Taylor, J. Electroanal. Chem. 27, 109, 201 (1970).
62. J.P. Carr and N.A. Hampson, "The Lead Dioxide Electrode", Chem. Revs. 72, 679 (1972).

63. D. Pavlov, C.N. Poulieff, E. Klaja and N. Iordanov, J. Electrochem Soc. 116, 316 (1969).
64. D. Pavlov, Electrochim. Acta 13, 2051 (1968).
65. P. Ruetschi, J. Electrochem. Soc. 120, 331 (1973).
66. P. Ruetschi and R.T. Angstadt, Ibid. 111, 1323 (1964).
67. T.G. Chang and M.M. Wright, "A Study of Quantitative X-Ray Diffractometry in the Quaternary System Pb(O)-PbO(T)-3PbO.PbSO₄.H₂O-4PbO.PbSO₄", Report No. 6, IRAP Project "Lead 162", February (1977).
68. T.G. Chang and M.M. Wright, "The Formation of Tetrabasic Lead Sulphate at 23°C", 150th Electrochem. Soc. Meeting, Las Vegas, Abstract #13, October 17-22 (1976).
69. A. Sabatino, Letter to K.V.N. Rao, Gould-Canada, 12 November 1976.
70. K. Murata and S. Hattori, "Advantageous Features of Microporous Thin Embossed Waffle Shape Separator", presented to Battery Council International, Washington, D.C., April 27 (1977).
71. P. Reinhardt, M. Vogt and K. Wiesener, J. Power Sources 1, 127 (1976/77).
72. J. Burbank, "Anodic Crystallization of Pure and Antimonial Lead in Sulphuric Acid", NRL Report 7256, May 24 (1971).
73. W.H. Tiedemann and K.R. Bullock, private communication.

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